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Au nanoparticle-decorated urchin-like TiO_2 hierarchical microspheres for high performance dye-sensitized solar cells

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ABSTRACT

Urchin-like TiO_2 hierarchical microspheres (UTHMs) with an extremely large surface area of 331 $m^2\,g^{-1}$ were synthesized via a facile one-pot hydrothermal method and studied for dye-sensitized solar cells (DSSCs) application. In-situ growth of Au nanoparticles (NPs) on the surface of the UTHMs were further conducted to achieve Au-decorated UTHMs (Au-UTHMs). A series of novel composite photoanode films were designed through the combined use of Au-UTHMs and UTHMs at different mass ratios. The DSSC constructed with the composite photoanode prepared under an optimal Au-UTHMs to UTHMs ratio of 2 wt% yields a considerable power conversion efficiency of 7.21%, which was markedly higher than that of the pure P25 NPs based device (5.19%) and pure UTHMs based device (6.10%). The significantly enhanced performance of the composite photoanode based DSSC can be attributed to the synergistic effect of two benefits: (1) the large specific surface area, strong light scattering and fast electron transfer channels arising from the novel hierarchical features of UTHMs, and (2) the enhanced light absorption owing to the localized surface plasmon resonance (LSPR) effect of Au NPs.

1. Introduction

Dye-sensitized solar cells (DSSCs) were first reported by O'Regan and Grätzel in 1991 and have aroused widespread attention owing to the attractive advantages including the simple fabrication, low cost and relatively high power conversion efficiency (PCE) [1,2]. To date, the highest efficiency reported for DSSCs has exceeded 14% [3]. The typical liquid DSSCs involve a sandwich structure that consists of three components: a photoanode, an electrolyte and a counter electrode [4–6]. As the vital part of DSSCs, the photoanode plays a critical role in light harvesting and charge transport. An ideal photoanode film of DSSCs requires high specific surface area for abundant dye adsorption, superior light scattering, as well as fast electron transport rate and slow recombination rate [7–11].

Since the large specific surface area facilitates the adsorption of dye molecules, small TiO_2 nanoparticles (NPs) (10–20 nm) have been extensively used as the photoanode materials for DSSCs [12]. However, the TiO_2 NP films usually exhibit high transparency and weak light scattering to visible light due to the small size of the NPs [13–15]. Moreover, the large amount of grain boundaries and disordered electron transfer channels in the TiO_2 NP films lead to low electron transfer and severe recombination losses [6,11,15,16]. Such disadvantages limit the further improvement of device performance. A number of attempts have been made to overcome these shortcomings. One-dimensional (1D) nanostructures (such as nanorods [17,18], nanowires [19,20], and nanotubes [21,22]) have been developed to accelerate the charge transport; however, the low specific surface area of 1D nanostructures results in the insufficient amount of dye [23,24]. Bi-layered and multi-layered photoanodes, typically involving the transparent nanocrystalline underlayer and the large-size particle overlayer, have also been extensively explored to reach superior dye adsorption properties and strong light scattering capabilities [11,25,26], while the preparation of multi-layered photoanode often requires a complicated process [4]. Therefore, many studies have been devoted to the development of multi-functional hierarchical materials self-assembled from NPs (0D), nanorods (1D) and nanoribbons (2D),

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with the aim of realizing high surface area, excellent light scattering and rapid electron transfer [11,15,25,27]. Urchin-like TiO_2 hierarchical microspheres (UTHMs), as a typical representative of multifunctional hierarchical materials, have attracted extensive attention in recent years [5,27–29]. For example, Liao et al. demonstrated a highly efficient (10.34%) DSSC based on UTHMs consisting of nanorods and NPs, and further elaborated the functions of the UTHMs [27]. A novel photoanode assembled with UTHMs for quasi-solid-state flexible DSSCs was developed by Fan et al. [5], yielding an enhanced PCE compared to that of the commercial P25 NPs based device.

Moreover, noble metal NPs (such as Au, Cu and Ag) have been incorporated into the photoanode of DSSCs to further increase the light harvesting capability [23,30–32]. Under the sunlight irradiation, free electrons in metal NPs collectively oscillate and localized surface plasmon resonance (LSPR) effect occurs [33]. The LSPR can intensify the local electromagnetic fields near the metal NP surface and enhance the light absorption of dye molecules in a specific waveband [34]. Among LSPR based photoanodes, Ag and Au NPs are the most widely used ones. However, Ag NPs might react with the redox-couple iodide/triiodide in the electrolyte to form AgI_2, leading to the poor chemical stability [35,36]; the LSPR peak of Ag NPs, located at 420 nm [23], is not well matched with the absorption peak of N719 dyes (around 515 nm). By contrast, the LSPR peak of Au NPs can be well matched with the absorption peak of N719 dyes, and Au NPs have better chemical and thermal stability than Ag NPs. Therefore, the construction of composite photoanodes by introducing Au NPs to realize the plasmonic enhancement is a promising strategy for increasing the light absorption of DSSCs.

In this work, we synthesized UTHMs with an amazing specific surface area (331 $m^2 g^{-1}$) via a facile hydrothermal method, and Au NPs were successfully loaded on the surface of the UTHMs (Au-UTHMs). The Au-UTHMs were mixed with UTHMs to fabricate composite photoanodes. It is found that the optimal Au-UTHMs to UTHMs ratio is 2 wt%, and the corresponding solar cell delivers a PCE of 7.21%, much higher than that of pure P25 NPs based cell (5.19%) and pure UTHMs based cell (6.10%). The performance improvement can be attributed to the composite photoanodes that holds large surface area, strong light scattering, and rapid electron transfer derived from UTHMs, and the LSPR enhanced light-harvesting ability thanks to the incorporation of Au NPs.

2. Experimental

2.1. Materials

Ethanol, diethylene glycol (DEG), (3-aminopropyl) trimethoxysilane (APTMS) and trisodium citrate were purchased from Sinopharm Chemical Reagent Corporation (China). Titanium oxalate ($K_2TiO(C_2O_4)_2$), urea (H_2NCONH_2) and Gold(III) chloride trihydrate were purchased from Aladdin Industrial Corporation (China). The Ru dye cis-diisothiocyanato-bis (2,2-bipyridyl-4, 4-dicarboxylato) ruthenium-(II) bis- (tetrabutyl-ammonium) (N719, >95%)was obtained from Solaronix SA (Switzerland). Titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol) were provided by Sigma-Aldrich (China). Both iodide/triiodide electrolytes and chloroplatinic acid slurry were purchased from Wuhan Jinge-solar Energy Technology Co. Ltd (China). All the reagents of analytical purity were used as received without further purification.

2.2. Synthesis of the UTHMs

The UTHMs were synthesized via a facile hydrothermal method according to Ref. [37] with some modifications. Typically, 22 mL of deionized water was added into the DEG solution (66 mL) under vigorously stirring for 5 min. Then, 2.3 g of urea and 0.78 g of $K_2TiO(C_2O_4)_2$ were added into the above solution undergoing continuous stirring for 1 h at room temperature. The precursor solution was then transferred into a Teflon-lined autoclave (100 mL) and kept at 180 °C for 10 h. The final products were centrifuged at 5000 rpm for 3 min followed by the collection of the pale yellow precipitates. After washed thoroughly with ethanol and deionized water for several times, the precipitates were dried at 60 °C overnight to obtain the UTHMs.

2.3. Preparation of the Au-UTHM composites

Au-UTHM composites were prepared through in situ growth of Au NPs (5–15 nm in diameter) on the surface of UTHMs resorting to the standard citrate reduction [31,38,39]. Typically, the as-synthesized UTHMs (0.20 g) were dispersed in 100 mL of absolute ethanol under ultrasonic vibration for 10 min. 500 μL of APTMS was added into the above solution under vigorously magnetical stirring for 4 h at 40 °C. The solution mixture were centrifuged at 5000 rpm for 3 min to obtain the APTMS-modified UTHMs, and washed with ethanol twice to remove the excess APTMS. The resultant product was redispersed into 100 mL of 0.127 mM $HAuCl_4$ solution under vigorously stirring for 30 min. The above solution was heated under continuous stirring until boiled. Then, a sufficient amount of sodium citrate was added into the boiling solution and the reaction lasted for 12 min. After the natural cooling, the resultant solution was centrifuged at 8000 rpm for 10 min, to obtain the Au-UTHMs, followed by thoroughly washing with ethanol and deionized water and drying in air. The as-prepared UTHMs and Au-UTHMs were further calcined at 500 °C for 3 h.

2.4. Fabrication of photoanodes and DSSCs

A series of paste were prepared to fabricate Au-UTHM composite photoanode. At first, 0.30 g of ethyl cellulose (EC) was dissolved in 5 mL of ethanol under vigorously stirring for 4 h at 70 °C, followed by adding terpineol (0.9 g) and acetic acid (0.2 mL). Then 0.3 g of TiO_2 powders (Au-UTHMs/UTHMs mixture, pure P25 NPs or pure UTHMs) were added into the above mixture, followed by alternatively magnetic stirring for 3 min at room temperature and ultrasonic treatment for 3 min. Finally, the removal of ethanol was performed on a rotary-evaporator to achieve a viscous paste.

For the preparation of a compact TiO_2 layer, 0.15 M of titanium diisopropoxide bis (acetylacetonate) (75 wt% in isopropanol) in ethanol solution was spin-coated onto the pretreated cleaned fluorine doped tin oxide (FTO) glass substrates, and further annealed at 500 °C for 30 min. Then the as-prepared paste was deposited onto the compact layer by using the doctor-blading technique to form absorbing layers, followed by annealing at 150 °C for 20 min, at 375 °C for 10 min, at 450 °C for 20 min, and at 500 °C for 30 min in air to remove the organic compounds. The resulted composite films were then immersed into 40 mM $TiCl_4$ aqueous solution in a closed vessel for 30 min at 75 °C, and then annealed at 500 °C for 30 min in air. After cooled down to 60 °C, the electrodes was soaked in 0.5 mM N719 dye in acetonitrile/tert-butanol (volume ratio 1:1) and kept for 24 h under dark. The dye-sensitized photoanode and the Pt-coated counter electrode were packaged together by heat sealing. The redox electrolyte, consisting of 0.1 M lithium iodide, 0.05 M iodine, 0.6 M 1, 2-dimethyl-3-propyl-imidazolium iodide and 0.5 M 4-tert-butylpyridine in dehydrated acetonitrile, was injected into the cell through a hole made on the counter electrode. The effective area of the DSSCs is 0.196 cm^2.